PB81-129579

Phthalate Ester Hydrolysis
Linear Free Energy Relationships

(U.S.) Environmental Research Lab.
Athens, GA

1980

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1. REPORT NO. EPA-600/J-80-016	2. JOURNAL ARTICLE
3. PB81-129579	
4. TITLE AND SUBTITLE Phthalate Ester Hydrolysis: Linear Free Energy Relationships	5. REPORT DATE
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) N.L. Wolfe, W.C. Steen and L.A. Burns	8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Environmental Research Laboratory U.S. Environmental Protection Agency College Station Road Athens GA 30613	10. PROGRAM ELEMENT NO. A28B1A
	11. CONTRACT/GRANT NO.
12. SPONSORING AGENCY NAME AND ADDRESS U.S. Environmental Protection Agency--Athens GA Environmental Research Laboratory College Station Road Athens GA 30613	13. TYPE OF REPORT AND PERIOD COVERED Journal Article
	14. SPONSORING AGENCY CODE EPA/600/01

15. SUPPLEMENTARY NOTES

Chemosphere. 9(7-8):403-408, 1980. Contact: N.L. Wolfe, 8-250-3428

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17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Phthalates Hydrolysis Models	Linear Free Energy Relationships Environmental Chemistry Water Solubility	02A 02C 02F 02M 07C

18. DISTRIBUTION STATEMENT RELEASE TO PUBLIC	19. SECURITY CLASS (This Report) UNCLASSIFIED	21. NO. OF PAGES 6
	20. SECURITY CLASS (This page) UNCLASSIFIED	22. PRICE

EPA Form 2220-1 (9-73)

REPRODUCED BY
NATIONAL TECHNICAL INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA 22161

Chemosphere Vol. 9, pp 403 - 408
Pergamon Press Ltd. 1980. Printed in Great Britain

0045-6535/80/0801-0403$02.00/0

EPA-600/J-80-016
Journal Article

PHTHALATE ESTER HYDROLYSIS: LINEAR FREE ENERGY RELATIONSHIPS

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ABSTRACT -- Alkaline hydrolysis rate constants were measured for dimethyl, diethyl, di-n-butyl, di-iso-butyl, and di-(2-ethylhexyl) phthalate esters in water. A linear free energy relationship (LFER) was established for estimating alkaline hydrolysis rate constants for other phthalate esters. Dimethyl phthalate hydrolyzes to phthalic acid with the mono ester as an intermediate. The rate ratio for the second-order-alkaline hydrolysis rate constants of the diester to the monoester is 12. Water solubilities for dimethyl, diethyl, di-n-butyl, di-n-octyl and di-(2-ethylhexyl) phthalate esters were measured and compared with literature values.

INTRODUCTION

Phthalate esters, although not generally introduced directly into the environment, are among the most ubiquitous of all manmade chemicals as evidenced by reports that show certain phthalates to be present in the water column, sediment, and biota as well as in aquatic vertebrates.[1,2] In view of the fact that approximately 1 billion pounds of phthalate esters were produced in 1976, it is surprising that so few published reports deal with the fate and transport[3] of these chemicals. Recent efforts[4] to estimate chemical reactivity and physical properties of organics in water by linear free energy relationships (LFERs) coupled with a recent survey showing the widespread distribution of phthalate esters in the ocean have prompted this report.[1]

Hydrolysis should be considered as a potential degradative pathway of phthalate esters in aquatic ecosystems. Any assessment of the fate and transport of these esters requires kinetic expressions for the hydrolysis processes and the corresponding rate constants. The kinetic expressions can be deduced from previous studies in organic solvents. Rate constants in water, however, are not available. Although the phthalate esters all have the 1,2-dicarboalkoxy structure in common, the large range of chain length and branching of the alkoxy moiety suggests a wide variation in rate constants within this class of compounds. Values for the rate constants are not always available, but a reliable estimate of the constant can often be quite acceptable for assessment purposes.

Structure-reactivity relationships can be useful in estimating some of the constants that are needed to evaluate the environmental behavior of certain organics.[5] In this report, alkaline hydrolysis rate constants are given for five phthalate esters and a LFER is established. Also, water solubilities of these esters were measured because these values in conjunction with established LFERs permit estimates of other physical constants such as octanol-water partition coefficients (K_{OW}), sediment-water partition coefficients (K_{OC}), and biosorption coefficients (K_B) that are useful in fate assessment.

MATERIALS AND METHODS

All phthalate esters were purchased commercially and used as received.

Second-order alkaline hydrolysis rate constants (k_{OH}) were determined following a procedure already described.[6,7] Hydrolysis studies were carried out at 30.00 ± 0.05°C never exceeding 10^{-5}M and always below the water solubility of the esters. The hydroxide ion concentration was fixed using standard solutions of sodium hydroxide of 0.01 to 0.0001M. The concentration of the esters was determined at given time intervals by extraction of an aliquot with benzene and analysis of the organic layer by glc (3% SE-30, electron capture) or by quenching the reaction with acid and analyzing by LC(ODS -50% methanol-water, uv detector - 230nm). The concentration of the mono and diacid products formed in dimethyl phthalate hydrolysis was determined by LC analysis (SAX - 0.2M KH_2PO_4, uv detector - 230nm).

Solubility determinations were carried out by stirring a minimum amount of the ester into 100ml of water. At 24-hour intervals, duplicate samples were removed and centrifuged at 15,000 RPM for 10 to 30 minutes. An aliquot of the supernatant was extracted with isooctane and the concentration in the organic layer was determined by glc analysis.

RESULTS

Hydrolysis studies of phathalate esters have not previously been done in pure water probably because of the low water solubility of many of the esters and the lack of a sensitive method of analysis. Second-order-alkaline hydrolysis rate constants (k_{OH}) for dimethyl- (DMP), diethyl- (DEP), di-n-butyl- (DNBP), di-iso-butyl- (DIBP), and di-(2-ethylhexyl)- (DEHP) phthalate esters are given in Table 1. These esters were selected for study because they represent extremes of the alkyl moieties in terms of chain length and branching and thus are the most useful esters in establishing a LFER. The reactivity of the esters varies with structural change of the alkyl groups with the second-order rate constant varying about three orders of magnitude and decreasing with an increase in chain branching.

Table 1. Second Order Alkaline Hydrolysis Rate Constants for Phthalate Esters at 30°C in Water

Ester	k_{OH} M^{-1} sec^{-1}[a]	σ^*[b]	E_s[b]
Dimethyl[c]	$(6.9 \pm 0.3) \times 10^{-2}$	0.00	0.00
Diethyl	$(2.5 \pm 0.2) \times 10^{-2}$	-0.100	-0.07
Di-n-butyl	$(1.0 \pm 0.05) \times 10^{-2}$	-0.130	-0.39
Di-iso-butyl	$(1.4 \pm 0.2) \times 10^{-3}$	-0.125	-0.93
Di-(2-ethylhexyl)	$(1.1 \pm 0.1) \times 10^{-4}$	-0.225	-1.13

[a]Mean value of two determinations and the average deviation. [b]Values from Taft.[10] [c]The second-order rate constant at 18°±1° in 1.0×10^{-3}M NaOH was $(3.1 \pm 0.3) \times 10^{-2} M^{-1} sec^{-1}$.

Water solubilities (S) are given in Table 2 for DMP, DEP, DNBP, DEHP, and di-n-octyl phthalate (DNOP) esters investigated in this study. These esters were selected primarily because of their widespread use and because they present a good cross section of phthalate water solubilities and the probable extremes in environmental fate behavior. Solubilities vary about three orders of magnitude and decrease, as anticipated, with an increase of the number of carbon atoms in the alkyl chains.

Table 2. Water Solubilites of Selected Phthalate Esters

Ester	Water Solubility	
	Literature[a] (mg/l, 20°)	Experimental[b] (mg/l, 25°)
Dimethyl	5000	4320 ± 37
Diethyl	1000	896 ± 20
Di-n-butyl	4.5	13 ± 1.6
Di-n-octyl	50	3.0 ± 0.5
Di(2-ethylhexyl)	Insol.	0.40 ± 0.05

[a]Taken from Fishbein and Alboro[12] at 20°. [b]Mean value and standard deviation, measured in this study at 25±2°.

DISCUSSION

Hydrolytic reactivity

The use of structure-activity relationships in studies of toxicology and bioconcentration is receiving increasing attention by environmental scientists as it becomes necessary to predict the impact of new compounds in the environment even prior to their manufacture and use.[8] Unfortunately, environmental chemists have not exploited the potential of these relationships for estimating rate constants for abiotic degradative processes for either individual compounds or to evaluate the chemical reactivity of classes of compounds.

The need to assess the hydrolytic fate of the phthalate esters prompts the use of a LFER to estimate the necessary hydrolysis rate constants.[9,10] Of the three hydrolytic pathways, only second-order alkaline hydrolysis needs to be addressed[11] because neutral hydrolysis is generally too slow to be detected and acid catalyzed hydrolysis is generally much slower than alkaline hydrolysis. For example, the second-order rate constant ratio of alkaline hydrolysis (85% ethanol-water) to acid hydrolysis (65% ethanol-water) is about 10^3 for ethyl benzoate at 25°.[11]

The overall reaction scheme for alkaline hydrolysis of phthalate esters is given in Figure 1 where R is any alkyl or aryl moiety and the disappearance rate expression, as shown by other investigators working with mixed water organic solvents,[11] is:

$$-\frac{d\,[\text{Phthalate}]}{dt} = k_{OH}\,[\text{Phthalate}]\,[OH^-] \qquad (1)$$

where k_{OH} is the second-order rate constant.

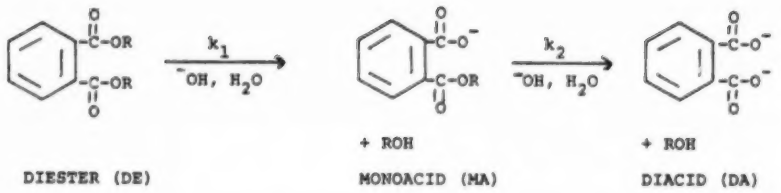

Figure 1. Reaction pathway for the alkaline hydrolysis of phthalate esters.

In the kinetic studies of dimethyl phthalate (DMP) in which the concentration was determined by LC analysis it was possible to monitor the formation of the mono- and diacid hydrolysis products. Figure 2 is a plot of concentration versus time for the disappearence of the dimethyl ester, the formation and disappearance of the monoacid, and the formation of the diacid products. Using the rate constants given in Figure 2, the ratio of the disappearence rate constant for DMP to that of the disappearence rate constant for the half ester (k_1/k_2) is determined to be about 12. To a reasonable approximation, this ratio would be applicable in assessing the hydrolysis of other phthalate half-esters.

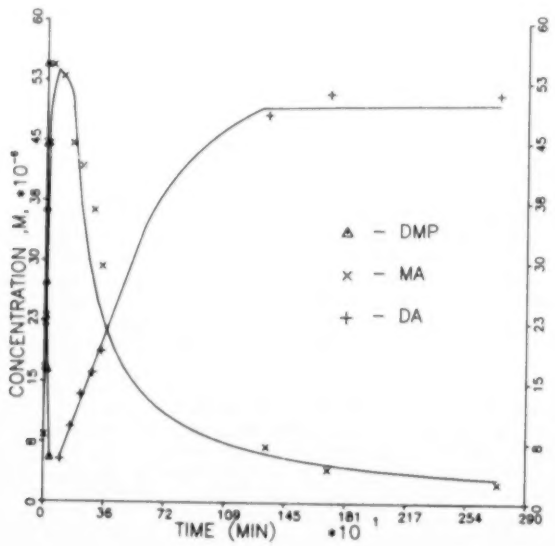

Figure 2. Plot of concentration versus time for the disappearance of dimethylphthalate (DMP), the formation and disappearance of the monoacid (MA), and the formation of the diacid (DA) at 30° in 0.01M NaOH, $k_1 = 6.9 \times 10^{-2}$ M^{-1} sec^{-1} and $k_2 = 2.9 \times 10^{-3}$ M^{-1} sec^{-1}.

The data base for the correlation of the phthalate esters is given in Table 1. The hydrolysis data were correlated using different equations as described by Shorter[9], but the Taft-Hancock equation 2 gives a satisfactory correlation and is straight forward to use.

$$\log k = \sigma^* \rho^* + \delta E_s + \log k_o \qquad (2)$$

In equation 2, k_o and k are the second-order alkaline hydrolysis rate constants for the methyl and larger alkyl group, respectively, ρ^* is a measure of the sensitivity of the reaction to changes in electronic effects, σ^*, and δ is a measure of the sensitivity of the reaction to steric effects, E_s. Linear regression analysis gives:

$$\log k = 4.59\ \sigma^* + 1.52\ E_s - 1.02 \qquad (3)$$
$$R^2 = 0.975$$

It should be pointed out that, although the values for σ^* and E_s are not generally listed in the tables of reference for longer alkyl chains, going from a n-C_5 to a n-C_8 alkyl chain should not significantly affect the values of the σ^* and E_s constants.[9] Thus for any alkyl chain containing more than five carbon atoms, adequate values can be deduced from the table of reference.

Water Solubility

The water solubility was determined for five selected phthalate esters. These esters were selected primarily on the basis of chemical structure and extent of distribution. The values are reported in Table 2 along with literature values as summarized by Fishbein and Albro.[12] For the low molecular weight esters, agreement is reasonable. As the water solubility decreases, the discrepancy increases.

These physical constants can be used in conjunction with existing LFERs to estimate useful physical constants such as sediment-water partition coefficients[13] and biosorption constants.[14] Use of these relationships in the fate and transport assessment of phthalate esters has been made by Wolfe and co-workers.[15]

CONCLUSIONS

The LFER established for the phthalate esters suggests that hydrolysis half-lives of the longer or branched alkyl esters will be long at alkaline pH concentrations characteristic of aquatic ecosystems. At pH 8 and 30° the calculated half-lives vary from 4 months for DMP to over 100 years for DEHP. These rate constants permit a comparison of the hydrolytic reactivity for the esters and the calculation of the maximum hydrolysis half-life at a given pH but do not provide any insight into the contribution of hydrolysis in an aquatic ecosystem. This is because the contribution of hydrolysis as a fate process is also influenced by other fate and transport processes. To describe the hydrolytic behavior of the phthalates under reaction conditions characteristic of aquatic ecosystems requires a systems approach.

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(Received in USA 15 June 1980)